

1

3,838,108

ISOCYANATE EXTENDED POLYMERS AND THE FORMATION OF BLOCK COPOLYMERS**William L. Hergenrother and Richard J. Ambrose, Akron, Ohio, assignors to The Firestone Tire & Rubber Company, Akron, Ohio****No Drawing. Filed Jan. 19, 1972, Ser. No. 219,161****Int. Cl. C08g 22/00, 41/04****U.S. Cl. 260—77.5 CR****86 Claims****ABSTRACT OF THE DISCLOSURE**

Polymers of anionically polymerized monomers are made with an organo alkali metal initiator and then reacted with either polyisocyanates or polyisothiocyanates which remove the alkali atoms and form a novel polymeric composition containing isocyanate or isothiocyanate terminated polymers. These polymers may then be reacted with compounds containing an isocyanate or an isothiocyanate reactive group. The isocyanate or isothiocyanate terminated polymers under anhydrous polymerization conditions may also be blocked with nylon forming monomers to form various nylon block copolymers. The isocyanate or isothiocyanate terminated polymers of the polymeric composition when reacted with urea forming monomers produce urea block copolymers. Reaction of the isocyanate or isothiocyanate terminated polymers with urethane forming monomers will produce urethane block copolymers. The isocyanate and isothiocyanate terminated polymers of the polymeric composition when reacted with imide forming monomers produce imide block copolymers.

BACKGROUND OF THE INVENTION

The present invention relates to the formation of polymeric compositions containing polymers terminated by either an isocyanate or an isothiocyanate. The invention also relates to the reaction of these polymers with a compound containing an active hydrogen. In another aspect, the present invention relates to the formation of nylon block copolymers by reacting the isocyanate or the isothiocyanate terminated polymers with nylon forming monomers. In yet another aspect, the present invention relates to the formation of urea block copolymers by reacting the isocyanate or the isothiocyanate terminated polymers with urea forming monomers. In yet another aspect, the present invention relates to the formation of urethane block copolymers by reacting the isocyanate terminated polymers with urethane forming monomers. In yet another aspect, the present invention relates to the formation of imide block copolymers by reacting the isocyanate or the isothiocyanate terminated polymers with imide forming monomers.

The polymerization of conjugated dienes and/or vinyl substituted aromatic compounds with organo alkali metal initiators is well known in the art. The resulting alkali metal terminated polymers often are reacted with polyfunctional compounds to couple the polymers. For example, as disclosed in U.S. Pats. Nos. 3,135,716 and 3,468,972 coupling agents which may be polyisocyanates or polyisothiocyanates are employed to replace terminal alkali metal atoms and to couple the polymers. In another U.S. patent, No. 3,225,119, isocyanates are reacted with the alkali metal terminated polymers to form an A-B-A type block polymer wherein A represents a polymer made from isocyanate monomers. In yet another U.S. patent, No. 3,281,383, compounds having at least three functional groups such as the polyisocyanates are coupled through the reaction with alkali metal terminated polymers to yield "radial" or multiple long branched polymers. None of these patents, however, disclose the preparation of anionically polymerized polymers which are terminated by

2

isocyanates or isothiocyanate groups. Furthermore, anionic polymers used in the preparation of block copolymers having a constituent other than the polymer or which constituent is made solely from isocyanate monomers are not disclosed.

Prior U.S. patents, Nos. 3,291,859 and 3,396,210, disclose a polymeric moiety which is formed by reacting a polymer which contains at least one active hydrogen with a polyisocyanate containing material. However, these patents do not disclose a base polymer which lacks an active hydrogen and yet is bonded to a polyisocyanate. The 3,291,859 patent also discloses that the polymer moiety can be used for making a block copolymer but only when a dual functional free-radical initiator is used.

Another aspect of the prior art relates to the desirability of using nylon as a molding resin for specific end use requirements. The nylon used often had a relatively low molecular weight in order that the nylon would possess the low melt viscosities necessary to fill molds rapidly. However, the use of low molecular weight nylon is undesirable since often toughness, which increases with molecular weight, is sacrificed.

Yet another aspect of the prior art relates to the use of urea polymers for specific end use requirements. However, these polymers generally are not processable at temperatures below the melt temperature of the polymer.

Yet another aspect of the prior art relates to the use of urethane polymers for specific end use requirements. However, these polymers generally are not processable at temperatures below the melt temperature of the polymer. Another aspect of the prior art relates to a thermoplastic urethane elastomer which is a block copolymer but is only processable above its melting point.

Yet another aspect of the prior art relates to the use of imide polymers for specific end use requirements. However, these polymers generally cannot be molded, milled or processed at temperatures below the melt temperature of the polymer.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to produce anionic polymerized polymers which are reacted with either polyfunctional isocyanates or polyfunctional isothiocyanates to provide a polymeric composition containing isocyanates or isothiocyanate terminated polymers.

It is also an object of the present invention to produce isocyanate terminated or isothiocyanate terminated polymers which are reacted with active hydrogen compounds.

It is another object of the present invention to provide a new nylon block copolymer by reacting an isocyanate or isothiocyanate terminated polymer with nylon forming monomers.

It is yet another object of the present invention to provide a nylon block copolymer which has rubbery properties or is suitable as a thermoset and yet otherwise generally retains the properties characteristic of nylon.

It is a further object of the present invention to provide a nylon block copolymer which is readily molded below the melt temperature of the nylon constituent.

It is another object of the present invention to provide a new urea block copolymer by reacting an isocyanate or an isothiocyanate terminated polymer with urea forming monomers.

It is yet another object of the present invention to provide a new urea block copolymer which has processable properties at temperatures below the melt temperature of the urea constituent.

It is another object of the present invention to provide a new urethane block copolymer by reacting an isocyanate terminated polymer with urethane forming monomers.

It is yet another object of the present invention to provide a new urethane block copolymer which has process-